## (19) Japanese Patent Office (JP)

(12) Official Gazette for Examined Patents (B2)

(11) Kohoku Patent No. 55[1980]-30,260

(24) (44) August 9, 1980

(51) Int. CI.<sup>3</sup> H 01 M 4/62 4/12 4/26

**Identification Symbols** 

Internal File Numbers

6821-5H 6821-5H 2117-5H

Number of Inventions: 1

(Total of 4 Pages)

(54) Method of Producing Negative Electrode [Anode] for Alkaline Battery

(21) Application No. 47[1972]-43724

(22) Filing Date: May 4, 1982

Kokai Patent No. 49[1974]-4135

(43) Kokai Date: January 14, 1974

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### (57) Scope of Patent Claim

1. A method of producing a negative electrode [anode] for an alkaline battery, characterized in that zinc in powder, fiber, or particle form is uniformly mixed and dispersed in an aqueous polyvinyl alcohol solution containing 0.01 to 10 mol% of a boron oxide or boric acid in terms of the polyvinyl alcohol, this mixture is molded, and then it is combined with an alkaline solution to produce a gel-like dispersion.

#### Detailed Description of the Invention

The present invention relates to a method of producing a negative electrode [anode] for an alkaline battery that uses metallic zinc as the anode active substance and oxygen or a metal oxide as the positive electrode [cathode] active substance.

As illustrated, this type of alkaline battery is usually obtained by joining an oxygen electrode for air batteries or a cathode substance 2, whose cathode active substance is a metal oxide, such as manganese dioxide, silver oxide, nickel oxide, or mercury oxide, to the wall around the inside of metallic container 1, which serves as the positive pole collector ring, further placing on the inside an anode substance 4 comprising a mixed gel of zinc in powder form, fiber form, or particle form as the negative pole active substance and a viscous substance, such as an aqueous carboxymethylcellulose solution or alkaline solution, with porous diaphragm 3, such as a nylon nonwoven material, in between, and connecting anode collector ring 5, which is inserted into this negative electrode substance, to anode 7 at the outside of seal 6.

This anode substance is a viscous gel-like dispersion and precautions must be taken so that it does not become fluid or change shape, that contact with the collector

ring does not deteriorate, and that the zinc does not separate during storage and use. Therefore, measures are taken such as dispersion in an alkaline solution of carboxymethylcellulose and adjusting the thickness of the gelling agent or the amount of zinc dispersed, or filling and sealing with no spaces remaining in a porous diaphragm pouch separated from the cathode substance, and the like. However, with long-term storage, the zinc particles do separate from the dispersion and the contact with the collector does deteriorate, resulting in shortening of the battery life and therefore, these measures are not satisfactory.

Moreover, the zinc ions that are produced during discharge of secondary batteries in particular elute into the electrolyte that impregnates the negative pole substance and porous diaphragm. Therefore, contact with the negative pole collector ring becomes poor and it is difficult to obtain a sufficiently high current and it becomes impossible to charge with a sufficient current. Moreover, the zinc that has eluted diffuses near the cathode substance to form zinc dendrites during discharge. These dendrites pass through porous diaphragm 3 and short-circuit the anode and the cathode, leading to a reduction in battery capacity and curtailment of battery life.

This anode substance undergoes considerable volume change during charging and discharging. Moreover, the dispersion is a liquid and therefore, it does not have the ability to retain its shape. Consequently, the porous diaphragm changes shape, particularly during volume contraction. This is accompanied by problems such as the contact becomes nonuniform between the anode and the porous diaphragm or the porous diaphragm and the anode substance, the internal resistance increases, energy

is lost through resistance polarization, the utilization factor decreases, a high current loading becomes impossible, and the like.

The present invention presents an improved alkaline battery with which these problems and others are eliminated. That is, the present invention is a method of producing an anode for an alkaline battery, whereby zinc in powder, fiber, or particle form is uniformly mixed and dispersed in an aqueous polyvinyl alcohol solution containing 0.01 to 10 mol% of a boron oxide or boric acid in terms of the polyvinyl alcohol, this mixture is molded, and then it is combined with an alkaline solution to make a gel-like dispersion.

This anode substance is characterized in that a zinc dispersion of crosslinked polyvinyl alcohol is obtained from a boron oxide or boric acid in place of the above-mentioned mixed gel with a viscous substance such as carboxymethylcellulose, sodium polyacrylate, water glass, and the like. The mixed gels that are currently used are primarily chain polymers as the base, and therefore, they are fluid and lack shape retention capability. In order to provide this shape retention capability, the gelling agent must be at a high concentration and this leads to a reduction in operating performance. Moreover, air bubbles readily mix in the negative pole substance, which leads to an increase in internal resistance and a reduction in battery properties. In addition, the majority of cross-linked polymers have poor ion conductivity and further, will not uniformly dissolve in aqueous alkaline solutions. Therefore, there is a tendency toward electrical insulation of the anode substance and the battery will not operate. Even if this is not the case, resistance to alkaline solutions is poor and battery life is curtailed.

Even though polyvinyl alcohol is an excellent diaphragm or gel and has high ion conductivity, it is a chain polymer and therefore, shape retention is difficult, battery life is short, and there is a reduction in the cycle life of secondary batteries and the utilization factor decreases. Therefore, by means of the present invention, 0.01 to 10 mol% of a boron oxide or boric acid is mixed with an aqueous polyvinyl alcohol solution, zinc is dispersed in this and molded, and then this is combined with an alkaline solution so that it is degraded with alkalinity and the polyvinyl alcohol crosslinks with the boron as the mediator to obtain a stable gel-like dispersion and this is used as the anode substance. If a boron oxide or boric acid is not used here, there will be a reduction in solubility of the polyvinyl alcohol when the polyvinyl alcohol degrades with alkalinity and although it will quickly gel as a result of hydrogen bonding, this solid will have very weak

shape-retention capability. In contrast to this, the >C-O-B-O-C bond where boron is in the middle is very strong and shape is retained with stability in alkaline solutions.

Furthermore, the boron atom at the center of the crosslinking has strong chain-forming affinity with zinc ions (Zn²+) and therefore, the elution of zinc ions into alkaline solutions that occurs as a result of discharge of secondary batteries in particular is avoided. Thus, the zinc particles are anchored semi-permanently at a certain position and maintain contact with the anode collector ring without moving. The gel dispersion does not deform and therefore, there is no increase in internal resistance, nor is there a reduction in the utilization factor, and an anode with excellent properties is obtained.

Next, an anode made from the gel dispersion obtained by the method of the present invention and an alkaline battery that uses the anode made by the method of the present invention will be described.

- (1) An aqueous solution of 3% boric acid was uniformly mixed with an aqueous 20% polyvinyl alcohol with a degree of polymerization of 4500 at weight ratio of 10:1 and then 60% of 50-mesh zinc powder was added to this and uniformly stirred at normal temperature. The dispersion that was obtained was poured into a nylon nonwoven pouch with a diameter of 10 mm and a brass rod with a diameter of 3 mm was inserted into this as the collector ring. Next, this filled pouch was immersed overnight at normal temperature in aqueous 40 wt% potassium hydroxide solution. The dispersion which was introduced in the bag became an elastic solid and it was confirmed to be a gel-like dispersion that retained its shape without changing for two years. When an aqueous solution of sodium hydroxide, barium hydroxide, rubidium hydroxide, cesium hydroxide, or lithium hydroxide was used in place of the potassium hydroxide and solidified by the same method, a gel-like dispersion that solidified in exactly the same way was obtained.
- (2) A sheet of a gel-like dispersion was used by the same method as described in Example (1). That is, after adding and uniformly mixing an aqueous 3 wt% boric acid solution with an aqueous 20 wt% solution of polyvinyl alcohol with a degree of polymerization of 500 at a ratio of 10:1, 55% of 100-mesh zinc powder was stirred in this at normal temperature. Then this was spread on a smooth saran sheet and a vinylon nonwoven material was placed on top to make a sandwich-like structure with a thickness of 2 mm to 3 mm between these two sheets. Next, an aqueous 30% sodium hydroxide solution was uniformly introduced over this vinylon sheet and then it was set aside overnight. A gel-like dispersion that was elastic and completely solidified was obtained overnight.

- (3) The same experiment was performed by the same method as in Example (1) with the exception that the degree of polymerization of the polyvinyl alcohol was varied from 50 to 3,000. A gel-like dispersion that was an elastic solid was obtained regardless of the degree of polymerization.
- (4) The mixture ratio of the polyvinyl alcohol and boric acid was varied to determine the limit with which an elastic solid is obtained. That is, various amounts of boric acid were added to an aqueous polyvinyl alcohol solution and then this was uniformly mixed. Next, 30 to 90 wt% of 100-mesh zinc powder was mixed with this and this was used as the gel for evaluation by the method in Example (1). This gel was set aside at room temperature. The lower limit of the mixture ratio was determined by the deflocculated state and the state of zinc separation, while the upper limit was determined from cracking and ion conductivity. As a result, the mixture ratio of boric acid to polyvinyl alcohol had a lower limit of 0.01 mol% and an upper limit of 10 mol%.
- (5) Studies were conducted using compounds other than the boric acid in (4) that provide boric acid ions, such as anhydrous boron oxide, meta-borates, and the like, but virtually the same result as with boric acid was obtained and it was clear that [these compounds] act to solidify the material into an elastic body. Moreover, it was clear that the same results are obtained with almost any component as long as the [given] molar percentage is used as the mixture ratio.
- (6) A battery was assembled as illustrated using the elastic gel-like dispersion obtained in Example (1) as the anode, enclosing the outside of this anode with cellophane, and using a nickel oxide cathode that was obtained by adding nickel oxide as the active substance to a nickel sintered compact. After placing an aqueous 35%

potassium hydroxide solution in between the two electrodes, the battery was sealed. This battery was discharged at 4  $\Omega$  and then charged at 1/2 C. This method was repeated. The results of comparing the life cycle of this battery with that of a conventional battery that used a uniform aqueous solution of 4% carboxymethylcellulose in placed of polyvinyl alcohol and boric acid are shown in Table 1.

Table 1.

	Number of cycles	10 Ahr	20	30	40	50	60	70
Capacity	Conventional battery	2.80	2.65	2.40	2.20	1.75	1.15	0.70
	Battery of the present invention	2.95	2.85	2.70	2.65	2.60	2.60	2.58

As is clear from Table 1, the battery of the present invention has a very long life when compared to the conventional battery.

(7) An anode of an elastic gel-like dispersion containing zinc powder that was made by the same method as in Example (1), with the exception that anhydrous boron oxide was used, and a cylindrical cathode substance that was made by uniformly mixing 5% zinc powder with silver oxide and molding under a pressure of 3 tons/cm² was used to assemble a battery of the same shape as shown in Figure 1. This was set aside at 65°C and the reduction in capacity was investigated. Furthermore, a silver oxide-zinc battery (Comparative Example) was made using the same conventional anode as described in Example (6) and the two batteries were compared by investigating the reduction in capacity after being similarly set aside at 65°C after they were discharged at constant resistance under a load of 4  $\Omega$ . As a result, in contrast to the fact that the

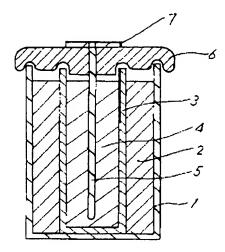
reduction in capacity of the battery of the present invention was 0.5 to 1.5% after five months and 2.5 to 4% after ten months, the conventional battery showed a reduction of 4 to 6% after five months and of 7 to 15% after ten months. The increase in the life of the battery of the present invention was considerable. Virtually the same result was obtained when metaboric acid and potassium metaborate were used in place of the anhydrous boron oxide.

- (8) An air-zinc battery was made after combining a conventional air battery electrode with the disc-shaped electrode made in Example (2), placing two pieces of vinylon nonwoven material in between these electrodes, and then thoroughly impregnating this with potassium hydroxide. The discharge properties were investigated with constant-resistance discharge under a load of  $50~\Omega$  after being set aside at  $65^{\circ}$ C. As a result, it was determined that 95% of the initial capacity was retained after ten months. However, a battery that used a zinc powder sheet made by conventional methods using carboxymethylcellulose showed a reduction in capacity of 77% of the initial capacity after the same storage time.
- (9) It was clear that the discharge properties are very good, even with the gellike dispersion of the present invention that uses zinc fibers in place of zinc powder. This is probably because in contrast to the fact that in the Conventional Example, the zinc fibers are nonuniformly worn with discharge, and some of the fibers therefore break, and then the broken fibers are displaced, resulting in deterioration of contact with the collector ring, the zinc is dispersed in an elastic solid when the gel-like dispersion of the present invention is used in the battery and therefore, there is no deterioration of contact due to displacement of zinc.

Thus, separation of the zinc particles and deformation of the gel-like zinc dispersion during long-term storage do not occur with the alkaline battery that uses the anode obtained by the method of the present invention. Moreover, the boric acid ions that are used as the crosslinking agent traps the Zn(OH)<sub>4</sub><sup>2</sup> with repeated charging and discharging when used as a secondary battery and this prevents the Zn(OH)<sub>4</sub><sup>2-</sup> that is produced as a result of the discharge from passing through the separator and reaching the cathode side. Consequently, there is little Zn(OH)<sub>4</sub><sup>2</sup>- around the cathode and therefore, deterioration of the cathode is prevented, the formation of zinc dendrite crystals during charging is inhibited, and short-circuiting can be prevented. Furthermore, this gel-like zinc dispersion is an elastic solid and therefore, self-shape-retention capability is good and problems with a reduction in the utilization factor and the capacity, poor low-temperature properties, and the like do not occur as a result of a degradation of electrical contact caused by expansion and contraction. This gel-like zinc dispersion can be made as hard as necessary by adjusting the mixture ratio of the polyvinyl alcohol and boron oxide, and it can have any shape, such as sheet, cylindrical, or columnar shape, prior to being degraded with alkalinity.

# Brief Description of the Drawings

The drawing is a cross section of an example of an alkaline battery.



#### ⑩日本国特許庁(JP)

#### 報 (B2) 許 公 特 昭55-30260

5 Int.Cl.3

識別記号

庁内整理番号

20公公告 昭和55年(1980) 8月9日

H 01 M 4/62 4/12 4/26

6821 - 5 H6821-5H 2117-5H

発明の数 1

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(全4頁)

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図アルカリ電池用陰極の製造方法

額 昭47-43724 ②特

②出 願 昭47(1972)5月4日

公 開 昭49-4135

③昭49(1974) 1 月14日

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#### の特許請求の範囲

1 ほう素酸化物又はほう酸をポリビニルアルコ ールに対し 0.0 1乃至10モルパーセントを含有 維状又は粒状の亜鉛を均一に混合分散し賦型した 後、アルカリ溶液を併合しゲル状分散体とする事 を特徴としたアルカリ電池用陰極の製造方法。 発明の詳細な説明

この発明は金属亜鉛を陰極活物質として用い、 酸素又は金属酸化物を陽極活物質として用いるア ルカリ電池用陰極の製造方法に関するものである。

とのようなアルカリ電池は普通図に示すように 陽極集電子を兼ねる金属性容器 1 の内周壁に接し て空気電池用酸素極又は二酸化マンガン、酸化銀、30 カリ電池を提供するもので、即ちほう素酸化物も 酸化ニツケル、酸化水銀等金属酸化物を陽極活物 質とする陽極物質2を配置し更に内側にナイロン 不織布の如き多孔性隔膜3を介して粉末状、繊維 状又は粒状亜鉛である陰極活物質と例えばカルボ 調体との混合ゲル質から成る陰極物質4を配置し この陰極物質に挿入されている陰極集電子5を封

口体6の外側で陰極7に接続しているものである。 この陰極物質は粘稠ゲル状分散体で、保存中又 は使用中に流動して変形したり集電体との接触を 劣化したり亜鉛を分離することのないように配慮 5 を要する。このためカルボキシメチルセルローズ のアルカリ溶液中に分散させて分離を防ぎゲル化 剤の粘稠度や亜鉛分散量を調整し、或いは陽極物 質と隔てる多孔性隔膜袋中に充分に隙間なく充塡 して密封する等の工夫が施されている。しかし長 10 期保存中に分散体からの亜鉛粒子分離、集電体と の接触劣化にもとずく電池寿命劣化が発生してこ れ等の工夫は満足すべき域に達しない。

又特に二次電池では放電中に生成する亜鉛イオ ンが陰極物質及び多孔性隔膜に含浸されている電 外3名 15 解液中に溶出し陰極物質を変形するため、陰極集 電子との接触を不良にして大電流を得難くし、充 電時に充分な電流での充電を不可能にし、一旦溶 出した亜鉛が陽極物質近傍に拡散して充電時に樹 枝状亜鉛となつて多孔性隔膜3を通過して陰極両 するポリビニルアルコール水溶液中に粉末状、織 20 極を短絡するようになり電池容量減少寿命短縮を 招来するに到る。

> 更にこの陰極物質は充放電時に体積変化が著る しい上、分散体は液体状であるため形状保存能力 がないから特に体積収縮に際して多孔性隔膜を変 25 形し、陰極と多孔性隔膜又は多孔性隔膜と陰極物 質の接触を不均一にし内部抵抗を増大し抵抗分極 によつてエネルギーを損失し利用率を減少し大電 流負荷を不能にする等の欠点を併せるものである。

この発明はこれ等の欠点を除き改良されたアル しくはほう酸をポリビニルアルコールに対し 0.0 1乃至10モルパーセントを含有するポリビ ニルアルコール水溶液中に粉末状、繊維状又は粒 状の亜鉛を均一に混合分散し賦型した後、アルカ キシメチルセルローズ水溶液乃至アルカリ液の粘 35 リ溶液を併合しゲル状分散体とするアルカリ電池 用陰極の製造方法である。

との陰極物質は前述のカルボキシメチルセルロ

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ーズ或いはこの他ポリアクリル酸ナトリウム若し くは水ガラス等の粘稠体との混合ゲル質に代りほ う素酸化物もしくはほう酸により架橋されたポリ ビニルアルコールの亜鉛分散体が得られる点で特 徴を有するものである。現行の混合ゲル質はおお 5 むね鎖状高分子を基体とする為に流動性があり形 状保持能力に乏しい。もしこの形状保持能力を付 与しようとすればゲル化剤を高濃度に要して作業 性を低下させ、また気泡が混入し易くなり、内部 抵抗を大にして電池特性を低下させる。又架橋さ 10 れる高分子の大半はイオン伝導性が悪く更にアル カリ水溶液と均一に相溶しないため陰極物質を電 気絶縁する傾向を呈し電池の動作を不可能にする ものであり、そうでない場合でもアルカリ液に対 し耐久力が低いために電池寿命を短くするのであ 15 る。

ポリビニルアルコールは隔膜乃至はゲル質とし てすぐれ、イオン伝導性も高いけれども鎖状高分 子であるために形状保持が困難で電池寿命が短く 二次電池のサイクル寿命、利用率を低下する。そ 20 とでこの発明ではポリビニルアルコール水溶液に 予じめほう素酸化物もしくはほう酸を 0.0 1 乃至 10 モルパーセント混合しておき、亜鉛を分散さ せ賦型してからアルカリ溶液を併合しアルカリ性 に変性しポリビニルアルコールをほう素を仲立ち 25 として架橋し弾力ある安定なゲル状分散体を得さ せて陰極物質としたのである。こゝでもしもほう 素酸化物もしくはほう酸を用いないで ポリビニルア ルコールをアルカリ性に変性するとボリビニルア ルコールの溶解度の減少と水素結合にもとずくゲ 30 (3) 例(1)に示したと同一の方法であるがポリビニ ル化が起るがこの固体形状保持力は極めて弱い。 これに反しほう素を中間にした >C-O-B-O-C、 結合は極めて強固でアルカリ液中で安定に形状を 保持する。更に架橋中間にあるほう素原子は亜鉛 イオン ( Zn²+) との鎖体形成能力大であるから 35 (4) ポリビニルアルコールとほう酸との混合比に 特に二次電池で放電の結果生成した亜鉛イオンの アルカリ液への溶出を防ぐ。これ等の効果により 亜鉛粒子は半永久的に所定位置に固定され陰極集 電子との接触を不動に保ちゲル状分散体が変形し ないため内部抵抗の増加、利用率の減少等を生じた 40 くく性能のすぐれた陰極を備えるものとなる。

次に本発明方法で得られるゲル状分散体からな る陰極乃至、本発明方法により得られた陰極を用 いたアルカリ電池について述べる。

- (1) 重合度 4 5 0 0 のポリビニルアルコール 2 0 %水溶液にほう酸3%の水溶液を10:1の重 量割合で加え均一に混合したのち、常温でこれ に50メツシュの亜鉛粉を60%加え、均一に 攪拌しえられた分散体を10째径のナイロン不 織布袋に注ぎ、これに集電子として3㎜ダの真 **鍮棒をそう入した。ついでこの充塡された袋を** 重合割合で40%カセイカリウム水溶液に1昼 夜常温で浸せき併合したところ、充塡された分 散体は弾性ある固体となり、形状は2年間不変 に維持されるゲル状分散体となることが認めら れた。これと同様な方法でカセイカリウムのか わりにカセイソーダ、水酸化バリウム、水酸化 ルビジウム、水酸化セシウム、水酸化リチウム の水溶液を用いて固化せしめたところ、全く同 様に固化するゲル状分散体が得られた。
- (2) 例(1)において述べたと同様な方法でシート状 のゲル状分散体を使用した。すなわち、重合度 500のポリビニルアルコール重量割合20% 水溶液にほう酸重量割合3%水溶液を10:1 の比で加え均一に混合後常温でとれに100メ ツシユの亜鉛粉を55%加え均一にかきまぜた のち平にしいたサランシート上に流しこの上に ビニロン不織布をのせて、2枚のシートにより 2㎜~3㎜厚のサンドイツチ状シートを作る。 しかるのち、とのビニロンシート上に30%カ セイソーダ水溶液を充分に均一に補給しつつ一 昼夜放置する。一昼夜には完全に弾性的に固化 したゲル状分散体をうることができた。
- ルアルコールの重合度を50~3000まで変 えたものにつき同様の試作を行つたが、どのよ うな重合度でもゲル状分散体として弾性的固体 をうることができた。
  - つき検討し弾性固体をうる限界を知る検討を行 なつた。即ちポリビニルアルコール5%水溶液 にほう酸を各添加量を加えて添加したのち均一 に混合し、これに100メツシユ亜鉛粉末を 30~90 重量%で混合したのち、これを例(1) に示した方法で評価ゲル体とし、これを、常温 に放置して解膠状況および、亜鉛分離状況によ り最小限界を、またひび割れとイオン導電性調 査により上限をそれぞれ調べた。その結果ポリ

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ビニルアルコールに対するほう酸の混合量は、 下限が 0.0 1 モルパーセント、上限が 1 0 モルパーセントであつた。

- (5) 例(4)においてほう酸の代りに無水酸化ほう素、メタほう酸塩など他のほう素酸素イオンを与え 5 る化合物を使用して検討を行なつたが、ほゞほう酸と同様の結果がえられ、弾性体としての固化効果があることがわかつた。また混合比としてはモルパーセントをとる限り、大略どの成分を用いても同様の効果があることがわかつた。 16
- (6) 例(1)で得られた弾性あるゲル状分散体を陰極とし、この外側をセロフアン紙で包んだ上、二\*

※ ツケル焼結体に活物質として酸化ニツケルを含有させて成る酸化ニツケル電極を陽極として図面に示したごとき電池を組み立て更に、35パーセントカセイカリウム水溶液を両者間に介在させたのち封口し、これを用いて4Ω負荷の放電を行わせ、ついで1/2℃で充電を行ない、この方法をくり返し、これをポリビニルアルコール、ほう酸の代りに4%カルボキシメチールセルローズの粘稠水溶液を用いた従来の電池とり比較し、サイクル寿命を調べたその結果を第1

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#### 第 1 表

に示す。

6 0 7 0 40 5 0 サイクル数 1 0 2 0 3 0 2.80 2.65 2.40 2.20 1.75 1.15 0.70 従来電池 2.70 2.65 2.60 2.60 2.58 2.9 5 2.85

第1表から明らかなようにこの発明の電池は従来の電池に比し、極めて大なる寿命を有するこ 20 とがわかつた。

- (7) 無水酸化ほう素を用い、他は例(1)において述 べたと同様な方法で製造した亜鉛粉末を含む弾 性ある、ゲル状分散体の陰極、および酸化銀に 黒鉛粉末を5パーセント均一に混合して3ton 25 /cmiの圧力を用いて円筒状の陽極物質を製し、 これを用いて図1に示したと同様な形状の電池 を製造し、これを65℃に放置し容量の減少量 を調べた。なお例(6)に示したと同様な従来陰極 を用いて酸化銀-亜鉛電池(比較例)を製し、30 同様に65℃放置後における容量の減少量を4 Ω負荷の定抵抗放電により調べ両者を比較した。 その結果本発明の電池容量の減少量は5ヶ月後 で0.5~1.5%、10ケ月後で2.5~4%であ つたのに対し、従来のものは5ヶ月後で4~6 35 %10ケ月後では実に7~15%の減少量があ り、本発明の寿命増加効果は著るしいものがあ ることがわかつた。なお無水酸化ほう酸の代り にメタほう酸、メタホウ酸カリウムを用いても ほぼ同様の効果が得られた。
- (8) 例(2)において製した、平板状電極に従来の空 気電池電極を組み合せこの間に更に2枚のビニ ロン不織布を介在せしめ、これに十分なカセイ カリを含浸させたのち、空気-亜鉛電池を構成

し、65℃放置後における50Ω負荷の定抵抗 放電の放電特性を調べた。その結果10ケ月後 においても初期容量の95%パーセントの容量 を維持していることが判つたが、従来法により、 カルボキシメチールセルローズを用いて亜鉛粉 末シートを作つたものは、同じく貯蔵後、初期 容量の77パーセントの容量に減少していた。

(9) 亜鉛粉末の代りに、亜鉛繊維を用いたとの発明に使用のゲル状分散体でも極めてよい放電特性を示すととが明らかとなつた。これは、従来例では放電に伴い、亜鉛繊維が不均一に消耗してゆき、部分的に切断がおこり切断された部分が移動して集電子との接触が悪くなるのに反しとの発明の電池に使用のゲル状分散体では弾性ある固体中に分散されている為亜鉛の移動による接触不良がないためと考えられる。

35 この様に本発明方法により得た陰極を用いたアルカリ電池では、長期保存中に亜鉛粒子の分離やゲル状亜鉛分散体の変形を起すことがない。また、二次電池として用いる時の充放電繰返しに対しても架橋剤として使用されたほう素酸素酸イオンは 40 Zn(OH)4 ー の補促剤として作用するため、放電の結果生成した Zn(OH)4 ー がセパレータを通過して正極側へ到達するのを阻止する。その結果、正極近傍は Zn(OH)4 ー が少ないから陽極の劣化が防止されると共に充電中の樹枝状亜鉛結

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晶生成を抑制するから短絡劣化を防止出来る。更 にこのゲル状亜鉛分散体は弾性ある準固体である ため自己形状保存力が大で膨張収縮にもとずく電 円柱状に賦形も任意である。 気的接触の劣化による利用率、容量の低下、低温 図面の簡単な説明 特性不良等の欠点を招くことがない。そしてこの 5 図はアルカリ電池の一例の縦断面図である。 ゲル状亜鉛分散体はポリビニルアルコールとほう

素酸化物もしくはほう酸の混合比で固さを所望に 出来、アルカリ性に変性する前シート状、円筒状、

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